

L133,706



# PATENT SPECIFICATION

NO DRAWINGS

L133,706

Date of Application and filing Complete Specification: 9 Nov., 1965.

No 47542/65.

Application made in United States of America (No. 410,007) on 9 Nov., 1964.

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## ERRATA

SPECIFICATION NO. 1,133,706

Page 3 line 98 for "FeCe," read " $\text{Fe}_2\text{Ce}$ "  
Page 4 line 79 for "course" read "course"  
Page 8 line 80 for "capactior" read "capacitor"

THE PATENT OFFICE  
26 June 1970

R 125436/25

## PATENTS ACT 1949

SPECIFICATION NO. 1,133,706

The following amendments were allowed under Section 29 on 11 May 1970.

Page 1 lines 43 and 70, page 3 line 60, page 13 lines 11 and 39, page 14 line 49  
for "B" read "Br"

Page 1 lines 44 and 71, page 3 line 61, page 13 lines 12 and 40, page 14 line 49  
delete "O"

Page 3 delete line 42 insert "glass, a flexible polymer or paper."

Page 3 line 43 delete "wood"

Page 3 line 91 after " $\text{NiFe}_2\text{O}_4$ " delete ",  $\text{CuFe}_2\text{O}_4$ ,"

Page 3 line 99 delete " $\text{FeS}_2$ " insert " $\gamma$ —"

Page 3 line 100 delete " $\text{Co}_4\text{Zn}$ ,"

Page 3 delete line 102 insert " $\text{Mn}_2\text{Sb}$ ," " $\text{Mn}_2\text{Sn}$ ,"

Page 3 line 103 delete " $\text{BeFe}_2\text{O}_4$ ,  $\text{BaFe}_2\text{O}_4$ ,"

Page 3 line 104 delete " $\text{CdFe}_2\text{O}_4$ ," and " $\text{CuFe}_2\text{O}_4$ ,"

Page 3 line 105 delete " $\text{PbFe}_2\text{O}_4$ ,  $\text{SnFe}_2\text{O}_4$ ,"

Page 3 delete lines "108 and 107"

Page 3 delete lines "108, 109 and 110" insert " $\text{Co}_2\text{P}$ ,  $\text{Mn}_3\text{As}_2$  and  $\text{Mn}_5\text{P}_2$ ."

Page 3 line 120 for "dyeing" read "drying"

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Index at acceptance:—B6 CA7; C1 AN10A; H1 H(1, 2, 4, 5C2, 6A, 6B)

Int. Cl.:—G 03 g 3/00

## COMPLETE SPECIFICATION

## Improvements relating to Thermomagnetic Copying processes, and to materials for use therein

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a new thermomagnetic copying process.

It is known from U.S. Patent 2,793,135 that magnetic substances having relatively low Curie points when coated on a surface and then substantially uniformly magnetised can be selectively demagnetised by projecting heat, through copy to be reproduced, onto the magnetised surface. The still magnetised portions of the surface will retain a magnetic ink which is coated thereon and printed copies of the magnetic image can be obtained.

While the copying members disclosed by U.S. Patent 2,793,135 are useful in imagewise copying techniques, they are not sufficiently transmissive or, loosely, transparent to be useful in a reflex copying process. Reflex exposure involves the exposure of a copying member to a source of radiant energy, the copying member being placed between the energy source and the original to be copied whereby a copy of the original is formed on the copying member.

The invention provides a thermomagnetic copying process which comprises exposing to actinic radiation, by reflex exposure as hereinbefore defined from a document, a magnetic recording member comprising fine discrete particles of a size of 0.01 to 5.0 microns of a material capable of magnetisation to a hard magnetic state having an energy product  $(BH)_{\max}$  of 0.08—8.0 gauss oersteds  $\times 10^6$ , a remanence  $B_r$  of 500—21,500 gauss, a coercivity  $H_c$  of 40—6,000 oersteds and a Curie

temperature not exceeding 1,200° C., contained in a stratum carried by a support, the whole being transparent to a degree sufficient to transmit at least 2% of actinic radiation, the intensity of the exposure being such that in the areas corresponding to the more reflective areas in the document the temperature of the magnetic material is raised above its Curie temperature, while in the areas corresponding to the less reflective areas it remains below the Curie temperature, while maintaining the copying member in a state such that its magnetic state will change above, but not below, the Curie temperature, and reading out the resulting magnetic image.

The invention further provides a thermomagnetic copying process which comprises (1) placing over a document to be copied a magnetised recording member which has a substantial degree of transparency to actinic radiation and which comprises fine discrete particles of a size of 0.01 to 5.0 microns of a material capable of magnetisation to a hard magnetic state having an energy product  $(BH)_{\max}$  of 0.08—8.0 gauss oersteds  $\times 10^6$ , a remanence  $B_r$  of 500—21,500 gauss, a coercivity  $H_c$  of 40—6,000 oersteds and a Curie temperature not exceeding 1,200° C., contained in a stratum carried by a support.

(2) selectively demagnetising the magnetised stratum by exposing it to actinic radiation by reflex exposure as hereinbefore defined of intensity such that its temperature in the areas corresponding to the more reflective areas of the document is raised above its Curie temperature, causing such areas to be demagnetised to a degree proportional to the reflectivity of the reflective areas of the document, while the areas corresponding to the less reflective areas of the document retain their magnetisation substantially unchanged, and (3) reading out the resulting magnetic image.

Our co-pending Application No. 47558/65

[Price 4s. 6d.]

(Serial No. 1,133,707) describes and claims a thermomagnetic imaging process which uses the same magnetic recording member as used herein, and wherein the read-in is accomplished with the aid of radiation selectively impinged on the member (not by reflex exposure).

The term document is used herein in its broadest sense to include any writing, book, or other instrument conveying information with a sensible reflectivity gradient.

The support can be either rigid or flexible, but is preferably the latter. Preferably the discrete particles are 0.1 to 2 microns, in size and are dispersed in a polymeric binder to form a stratum 0.003 to 0.13 mm thick carried on a support.

The magnetic image formed can be developed by any one of several ways well known in the art, including the use of specifically magnetic sensing means, e.g. a conventional "sensing head" with the necessary coupled circuitry, including amplification and ultimate read-out by any one of several conventional means, including projection of an oscilloscope trace or television read-out. Alternatively, the image can be developed visually by simple exposure to a magnetic developing material, such as finely powdered metallic iron or other ferro-magnetic powder. The developed magnetic image can be read visually on the imagewise demagnetised copy member; right reading if viewed through the back, or alternatively it can be transferred therefrom by conventional techniques to an image receptor, e.g. white bond paper, preferably coated on one side, which is brought into direct contact with the uppermost surface of the developed member. The developed image is transferred to the image receptor to give a right-reading copy of the original. Other methods include the use of the Faraday effect on rotation of a sensing plane polarised light beam on transmission; sensing with an electron beam; utilising the Zeeman effect involving the break-up of the spectral lines of a light source in a magnetic field into two or more polarised components which viewed perpendicular to the field generally comprise three lines, the central one plane polarised at right angles to the field and having the original wave length, and the other two being plane polarised parallel to the field, one being shorter and the other longer in wave length than the original line, with the differences being the same in magnitude in both cases; the use of the Kerr effect involving the rotation of a sensing plane polarised light beam by reflectance; the use of a conventional magnetic tape viewer such for example as that described in U.S. Patent 3,013,206, with the further possible permutation that any such sensed image can also be viewed, preferably enlarged, by use of any one of several commercially available projectors.

Images can be developed and transferred according to procedures well known in the magnetic printing art. However, the type of image obtained will be greatly influenced by the type of magnetic toner used. Image resolution, uniformity, and quality are functions of the magnetic and electrostatic properties and also the particle size and size distribution of the toner.

For high resolution the toner particles should be small (3—5  $\mu$ ) but there should be, and normally will be, larger particles present also. The response of the toner to the magnetic fields of the image will be controlled in part by proper adjustment of the range of coercivity and saturation magnetisation of the toner particles as well as the electrostatic properties which may be used as a bias to aid in development and in the final toner transfer step.

The type of toner chosen will also depend on whether the final image is to be used in a magnetic read-out, which may require high permeability or high remanence material. The type of toner used (and throughout this discussion it should be appreciated that the term "toner" is used in the recognised sense of a material capable of developing a magnetic image) will also vary depending on the nature of the image receptor sheet. Thus, as described in detail in the Examples, if the image receptor sheet carries an, or is, adhesive, the image can be successfully transferred from the imagewise demagnetised sheet by simple pressure after the image is developed using suitable magnetic toner powder. On the other hand, if it is desired to transfer the image to a non-adhesive receptor sheet, e.g. conventional white bond paper, a different type of toner particle will be used; in such case the toner particles, whatever their nature, e.g. one of the iron oxides, will have been previously coated with a thermoplastic material such as a relatively low-melting polymer or copolymer which will be inert to magnetic fields. Thus, in this method, the developing toner powder will adhere to the imagewise demagnetised member and then can be transferred by a combined pressure and fusion step to white bond paper, giving a fixed right-reading positive image, the fixing being due to the thermoplasticity of the coating on the developing toner particles on heating.

It is to be understood that the present copying process depends for its operability on the presence of a reflectivity gradient in the original being copied, and that, similarly, the read-out techniques depend on the sensing of a magnetic gradient in the copying member after read-in. The reflectivity gradient in the original being copied results in a directly corresponding magnetic gradient in the copying member on exposure by virtue of the proportional demagnetisation of the copying member in the areas thereof corresponding to

the areas of greater reflectivity in the original being copied. The sensitivity required in each particular sensing means is a function of the relative magnitude of the magnetic gradient in the exposed copying member. Desirably, this magnetic gradient will be as large as possible, ideally varying from 100% demagnetisation in the most intensely exposed areas and 0% demagnetisation in the non-exposed areas. However, this need not necessarily be so, and the demagnetised read-in image can be sensed with magnetic gradients of relatively low percent difference in magnetisation, particularly with the more sensitive sensing means such as a magnetic read-out head or electron beam read-out. For the grosser less sensitive read-out techniques, such as toner development, it will be desirable to obtain as high a magnetic gradient between the most exposed and nonexposed areas as possible.

Desirably, the material capable of magnetization to the hard, magnetic state will be of particle size of one micron and under, although since most such magnetisable materials, by their very nature, tend to agglomerate, any one of magnetisable area will frequently contain agglomerates ranging in size possibly up to 0.25 mm. In recording and copying techniques, the resolution and the packing factor are both direct functions of the particle size of the working component, in that a bit cannot be efficiently recorded that is smaller than the particle size of the working component through which it is to be recorded. Accordingly, the smaller and more uniform the particle size of the material to be magnetised, the better.

The nature of the support in and/or on which the magnetisable stratum is positioned can vary widely; for example it may be of glass, a flexible polymer, paper, cardboard or wood. For most purposes a flexible polymeric support will be preferred. However, any flexible low heat-conducting material can be employed, including mica and the commercially available flexible glass substrate known in the trade as ribbon glass.

The thickness of the magnetisable stratum is important. For maximum resolution it should be from 0.0003 to 0.13, preferably 0.0013 to 0.05 mm. The thickness of a flexible support will generally be 0.003 to .25 mm, most usually 0.005 to 0.13 mm., thickness in the range 0.0013 to 0.05 mm. being especially preferred.

The magnetisable material must be capable of magnetisation such that it exhibits an energy product  $(BH)_{max}$  of 0.08—8.0 gauss oersteds  $\times 10^6$ , a remanence  $B$  of 500—

21,500 gauss, a coercivity  $H_c$  of 40—6,000 oersteds, and a Curie temperature not exceeding 1,200° C., preferably from 25° to 500° C. Desirable it should also have as high a satura-

tion magnetisation  $\sigma_s$  as is possible, consonant with the other properties indicated above. An especially preferred magnetisable material is chromium dioxide because it has three valuable properties, i.e. relatively high coercivity, relatively high remanence at room temperature, and a conveniently accessible Curie temperature. It can be used alone, i.e. in substantially pure form, or modified with one or more reactive elements. Descriptions of compositions which have the necessary properties and methods of making them can be found in the following U.S. Patents: 2,923,685; 2,956,955; 3,074,778; 3,078,147; 3,117,093 and British Patent 859,937. Essentially any well-known hard, magnetic material can be used in the present process. Of course, when the material has a relatively high Curie temperature, care must be used in selecting the binder and where applicable, also the substrate on which the magnetisable stratum is to be carried.

Representative other magnetic materials suitable for use in the invention include the ferrites; hard magnetic ternary alloys of Al, Ni and Co; ternary alloys of Cu, Ni and Fe,  $Mn_{1.5}FeTi_{0.5}O_4$ ,  $MnFe_2O_4$ ,  $Fe_3O_4$ ,  $CoFe_2O_4$ ,  $NiFe_2O_4$ ,  $CuFe_2O_4$ , and  $Li_{0.5}Fe_{2.5}O_4$ . Also suitable are hard magnetic ternary alloys of Cu, Ni and Co; chrome steel, cobalt steel, Fe, Co, Ni and General Electric Co. extended single domain magnetic iron materials (normally prepared in powder form and fabricated by conventional powder metallurgy) as well as  $Fe_3Al$ ,  $FeBe_2$ ,  $FeBe_3$ ,  $Fe_2B$ ,  $Fe_3C$ ,  $Fe_3Ce$ ,  $Fe_3N$ ,  $Fe_3P$ ,  $FeS$ ,  $FeS_2$ ,  $Fe_2O_3$ ,  $Fe_2P$ ,  $FeSi_2$ ,  $Co_2B$ ,  $CoS_2$ ,  $CoZn$ ,  $Co_2Zn$ ,  $Ni_2Mg$ ,  $Ni_3Mn$ ,  $MnAs$ ,  $MnB$ ,  $MnBi$ ,  $Mn_4N$ ,  $MnP$ ,  $MnSb$ ,  $Mn_2Sb$ ,  $Mn_3Sb_2$ ,  $Mn_2Sn$ ,  $Mn_3Sn$ ,  $AgF_2$ ,  $CrS_2$ ,  $CrTe$ ,  $Fe_3O_3S$ ,  $AlFe_2O_4$ ,  $BeFe_2O_4$ ,  $BaFe_2O_4$ ,  $CdFe_2O_4$ ,  $CoFe_2O_4$ ,  $CuFe_2O_4$ ,  $MgFe_2O_4$ ,  $MnFe_2O_4$ ,  $NiFe_2O_4$ ,  $PbFe_2O_4$ ,  $SuFe_2O_4$ ,  $SrFe_2O_4$ ,  $La_2O_3 \cdot Fe_2O_3$ ,  $Pr_2O_3 \cdot Fe_2O_3$ ,  $Nd_2O_3 \cdot Fe_2O_3$ ,  $Sm_2O_3 \cdot Fe_2O_3$ ,  $Er_2O_3$ , and  $Y_2O_3 \cdot Fe_2O_3$ ,  $FeSn_2$ ,  $Co_2As_2$ ,  $Co_2P$ ,  $NiHg_3$ ,  $Mn_3As_2$ ,  $Mn_3C$ ,  $Mn_3N_2$ ,  $Mn_3N_2$ ,  $Mn_3P_2$ ,  $MnS$ ,  $MnS_2$ ,  $MnSe$ ,  $MnTe$ ,  $CrAs$ ,  $Cr_2As$ .

Shape anisotropy or magneto-crystalline anisotropy can be used in the preparation of the image plates or films to obtain a preferred orientation of the magnetic particles either in the coating direction, or perpendicular to the surface of the film if the latter is so desired to give a greater optical transmission for reflex copying. Perpendicular orientation can be obtained by applying the magnetic composition in a solvent, and dyeing it in a perpendicularly applied field, or by using in place of a solvent in such an operation a thermoplastic binder at a temperature at which it is flowable, but which is still below the Curie temperature of the magnetic material, and cooling it, still in the perpendicularly applied field, e.g. to room temperature. Similarly parallel orientation can be obtained by drawing the magnetic stratum before it has set directly

across the pole pieces of a magnet oriented with its field axes in the direction of travel of the stratum.

On exposure, the radiation passes through the back of the support member, then through the magnetised stratum to the original to be copied, and finally back by imagewise reflection to the magnetisable stratum. The initial overall exposure thermally biases the magnetised stratum, and the radiation reflected back from the non-image (White) areas of the original demagnetises the stratum in the non-image areas.

The exposures can vary widely in intensity and duration and in the equipment used. It is only necessary that sufficient energy be available during the imagewise exposure to bring the temperature of the magnetised stratum above the Curie temperature of the magnetised component in the non-image areas, and that the exposures should be such that the low heat-conducting support and binder or matrix, if the latter is used, are not damaged physically, i.e. are not heated sufficiently strongly to impair significantly their physical properties.

The radiant energy used is preferably of such intensity that the exposure time is quite short. This not only serves to increase speed of replication, but also decreases any possible tendency for undesirable effects to arise in the binder or the substrate. Normally the radiant energy used will lie in the range 0.0001—2.0 watt -sec./cm<sup>2</sup>. and preferably 0.01—0.5 watt-sec./cm<sup>2</sup>. Usually the duration of exposure will be between one micro-second and 100 milliseconds; an average range is 0.1—10.0 milliseconds. The peak intensity of the radiant energy used in the exposure may be between 20 and 200,000 watts/cm<sup>2</sup>, and will normally be 200—100,000 watts/cm<sup>2</sup>. A preferred exposure source is a high voltage, high intensity photographic flash lamp, and in particular a xenon type lamp.

Another method to reduce exposure energy requirements may be useful with hard magnetic materials with Curie temperatures considerably above room temperature. This takes advantage of the gradual decrease in coercivity and in saturation and remanent magnetisation with increasing temperature. An AC erasing field of amplitude insufficient to cause loss of the magnetic signal at room temperature or at some elevated thermal biasing temperature is applied. Energy added imagewise from a flash tube will then elevate the temperature of certain areas of the film to a point where the applied erasing signal will exceed the coercivity of the magnetic particles with erasure of the magnetic signal according to the image information. Alternatively an unmagnetised film can be imagewise exposed in the presence of a magnetic field insufficient to magnetise the magnetic particles of the film at room temperature or at some elevated biasing temperature. The additional energy added by the

flash exposure must then heat the magnetic particles to the Curie temperature at which their coercivity is exceeded by the magnetic field applied. In this method the magnetic particles so heated become selectively magnetised to give a negative image after image transfer.

As previously indicated, the matrix or binder in which the magnetic material is dispersed is preferably flexible, not unduly sensitive to heat (i.e. stable to temperatures of 200°—400° C., and to the exposing radiation for short, i.e. millisecond, periods), and of low heat conductivity. In addition of course they must be non-reactive with the magnetic material and readily processable by conventional techniques such as solution milling, calendering or extruding. Suitable binders include commercially available acrylate and methacrylate, and functionally substituted acrylate and methacrylate polymers; vinyl and vinylidene polymers and copolymers, such as vinyl chloride/vinyl acetate, vinylidene chloride/vinyl acetate, and vinyl chloride/vinyl fluoride copolymers; olefin polymers and copolymers, such as polyethylene and polypropylene; ethylene/vinyl acetate copolymers, and ethylene/vinyl chloride copolymers.

Natural, modified natural, and other synthetic materials can also be used as binders or matrix materials provided they are unaffected by magnetic fields, not unduly sensitive to heat, and compatible (i.e. non-reactive) with the magnetic material. Examples of such materials include natural matrix materials as tung or China wood and linseed oils, the many well-known printing ink and lithographic type varnishes, the natural resins such as Copal, shellac and Damar gum; the drying oils, and many well-known alkyd-based varnish and drying oil-type formulations; the derived natural polymers such as regenerated cellulose; cellulose acetate, cellulose acetate propionate, cellulose propionate, cellulose acetate butyrate; the synthetic condensation polymers such as the nylons, e.g. polycaprolactam, polyhexamethylene adipamide, or like mixed ester/amides and synthetic condensation polymers derived therefrom such as polyhydroxymethyl polyhexamethylene adipamide; polyurethanes, e.g. that from ethylene glycol/adipic acid/tolylene diisocyanate, as well as the polyurethanes based on relatively high molecular weight addition glycols such as that from a polytetramethylene ether glycol (obtained by ring opening of tetrahydrofuran), adipic acid and tolylene or hexamethylene diisocyanate with, if desired, a finishing diamine, such as hexamethylenediamine; thermosetting resin binders or matrices, e.g., polyurea-formaldehyde and modified polyurea-formaldehyde compositions wherein the modifying component can be an amine such as hexamethylenediamine.

In addition to the foregoing largely or

wholly organic binders and matrices, suitable inorganic binders and matrices can be used, so long as they are transparent to the exposing radiation and meet the other requirements set out above. Suitable examples include the silico-

5 cones, aqueous colloidal silica sols, aluminum oxide films, and titanate films which can be dispersed and heat set or vapour deposited.

10 The magnetisable or magnetised stratum can be made a part of the recording member without use of a binder. For instance, a suitable "hard" magnetic material, e.g. chromium dioxide can be rubbed over the surface of a rigid support, e.g. glass, or a flexible support,

15 e.g. a polyethylene terephthalate film base. By this technique, in both instances the magnetic component by physical attrition is sufficiently embedded into the surface of the support so to cause enough to be retained in the support

20 to permit its use in the process. These physically applied magnetic strata can be made more resistant to handling by topcoating with a polymeric coating transparent to the read-in actinic illumination or a vapour-deposited

25 coating of a material which is non-magnetic and transparent to the read-in actinic radiation, e.g. titanium dioxide.

As already indicated, many materials are useful as the magnetic component. Preferably,

30 they should not only possess hard magnetic properties, low Curie temperature, high remanence and high coercivity, but also physically should be capable of formulation by conventional techniques into relatively fine particles,

35 preferably acicular, at dimensions approaching single domain dimensions. It is axiomatic that the information bit cannot be smaller than the smallest single domain particle size of the demagnetisable magnetic component.

40 The fine particles of the magnetic material normally exist, and therefore appear in the copying members, in agglomerated form. This tendency for agglomeration is believed to hold true whether the working component is in

45 magnetised or magnetisable form. In the former condition, this agglomeration tendency is probably most attributable to particle-particle magnetic interaction, and in the latter possibly to conventional Van der Waal's

50 physical interactions, which may also contribute to agglomeration in the magnetised state. Such agglomeration is positively advantageous, as favouring the transparency which is a necessary, but surprising feature of the copying

55 members of the invention. Within the degree of control possible therefore, it is preferred that the working magnetic component in the magnetic stratum of the copying member be non-homogeneously dispersed and be in "clumps"

60 or agglomerates significantly greater in size than single domain particles so as to improve the transmissivity of the copying member to the exposing radiation.

65 A number of factors contribute to the designation of a material as "hard" or "soft"

magnetically. Many magnetic materials usually designated as "soft" will show high coercive force when prepared as fine particles. Geometrical factors, including size and shape of the particle, are important. For example, iron is normally considered a "soft" magnetic material with a coercivity of a fraction of an oersted. However, small iron particles composed of single domains with long lengths compared to their diameters can be expected to show coercivities of the order of  $10^3$ — $10^4$  oersteds. In this case, high coercivity is due to shape anisotropy. For other materials, such as manganese bismuthide or cobalt, high coercivity for single domain particles may be the result of magnetocrystalline anisotropy arising from an easy direction of magnetisation along a particular crystalline direction. Even fine nickel particles should show a high coercivity under uniaxial stress. Many normally "soft" magnetic materials not in single domain form can be made to exhibit a high coercivity after being subjected to cold work or other similar treatments designed to introduce defects or internal strains which serve to pin or block movement of domain walls. Further discussion of "Hard Magnetic Materials" can be found in the article with that title by E. P. Wohlforth, *Advances in Physics*, supplement to *Philosophical Magazine* 8 (April 1959) pp. 87—224 and in the book by R. M. Bozorth on "Ferromagnetism", D. Van Nostrand and Company, Princeton, New Jersey (1951), particularly the section on fine particles, pp. 828—834. "Soft Magnetic Materials" are also discussed widely in the literature, e.g. E.W. Lee and R. L. Lynch, *Advances in Physics*, supplement to *Philosophical Magazine* 8 (July 1959) pp. 292—348. While successful copying has been achieved using copying members having as low as 2% transmissivity for the exposing radiation, involving as much as 60% demagnetisation, at these extremely low transmissivities the energy density necessary to achieve this degree of demagnetisation will be around 270 millijoules/cm<sup>2</sup>. At the other end of the scale transmissivities as high as 99% can be used successfully, provided that the magnetic stratum has a sufficiently high coercivity and remanence.

Normally speaking, the percent transmissivity of the copying member for the radiation used will lie in the range 5—95%, but the best results will be obtained when it is in the range 50—90%. The transmissivity of the copying member and the intensity of exposing radiation (and they necessarily are interrelated) will preferably be chosen so that the minimum intensity of exposing radiation as a function of the percent transmissivity will be as low as is consonant with the achievement of a demagnetised image of good contrast. Ideally then, the copying member will be so formulated that its transmissivity for the



exposing radiation is such that the energy density on exposure at the copying surface necessary to achieve significantly high percentages of demagnetisation, e.g. 80—100% and preferably 90—100% demagnetisation, will be achievable at energy density values at the copying surface no higher than 250 millijoules/cm<sup>2</sup> and preferably in the range 200—240 millijoules/cm<sup>2</sup>.

The material to be copied must of course exhibit a reflectivity gradient, i.e. there must be a difference in reflectivity between different areas. This holds true for all black on all white, which will be the situation for so-called line copy, and for varying degrees of black on varying degrees of white as well as varying concentrations of black and white, inclusive of, for instance, grey scale, pictorial, i.e. photographic negatives or positives or halftones. All of these can be faithfully copied in good resolution and detail by the present process, since the degree of demagnetisation in the copy member on exposure is proportional to the reflectivity in the corresponding area of the original being copied.

Coloured images in any area of the colour spectrum can also be copied. Development of such colour copied images and ultimate transfer and permanent copy can be effected similarly in any range of the colour spectrum by suitably choosing the colour of the developing toner powder. Thus as an example, a blue original can be copied by the techniques previously discussed using a blue toner to give a blue image, though a toner or developer powder of any other colour can be used if desired. Thus the blue original can be made to give a black-on-white copy by using a black developing toner powder, and more generally original of any colour, whether red, blue, green, or yellow, can be successfully copied and processed to give a black or a red or a green or a yellow final copy, as desired. A multi-coloured original, whether line or halftone, can be reproduced by making colour separation plates of the original, making demagnetised transfer plates of each of the colour separation plates, selectively developing each of these coloured separations with the appropriate coloured toner, and transferring all these images to a final copy sheet in register.

Imagewise recorded patterned information on a high coercivity tape (chromium dioxide tape, for example) can be printed onto a lower coercivity magnetic tape such as a conventional magnetic recording tape coated with  $\gamma$ -ferric oxide, for example by the method of M. Camras and R. Herr, Electronics 22 (December 1949) p. 78, in which an alternating magnetic field less than the coercivity of the imaged master is applied while the master and the lower coercivity tape on which a copy is to be made are in intimate contact.

The process and copying members can be

commercially used to make excellent thermographic copies by reflex exposure, the images of which can be read out visually, for example by projection or television, or transferred to an image-receptive support such as bond paper. Other read-out methods have been previously described.

The following Examples, in which parts given by weight, and in which reflex exposure as hereinbefore defined is used, illustrate the invention.

#### EXAMPLE I.

##### Part A — Preparation of CrO<sub>2</sub>.

The preparation of a magnetic CrO<sub>2</sub> species involved the precipitation of Cr<sub>2</sub>O<sub>3</sub> hydrate from a dilute solution of chromium nitrate using dilute ammonium hydroxide solution. The resultant precipitate was removed by filtration and air-dried to an approximate formula Cr<sub>2</sub>O<sub>3</sub> · 9H<sub>2</sub>O. The product was then dehydrated by heating in a muffle furnace at 600° C. for two hours. A blend was then prepared of 23 g. of the thus dried Cr<sub>2</sub>O<sub>3</sub>, 34.5 g. of CrO<sub>3</sub> crystals, and 14.4 cc. of water, which blend was then sealed in a platinum tube. The tube was then heated at 300° C. under 1,033.3 kg/cm<sup>2</sup> pressure for eight hours. The tube was then cooled, opened, and the resulting CrO<sub>2</sub> product removed, washed repeatedly with water on the filter, dried in acetone, and finally pulverized in an agate mortar. The magnetic properties of the thus obtained CrO<sub>2</sub> product included a coercivity of 370 oersteds, a saturation magnetization of 85 emu/g. at 4400 oersteds, 25° C., and a remanence ratio of 0.45.

##### Part B — Preparation of Thin CrO<sub>2</sub>-Containing Films.

A 15-part sample of magnetic CrO<sub>2</sub>, prepared as described in Part A, was ball-milled for 90 hours with 50 parts of a 5% by weight solution of high molecular weight polymethyl methacrylate in methyl ethyl ketone along with an additional 88 parts of methyl ethyl ketone to correct the viscosity. After ball-milling, a casting solution was prepared from 51 parts of the resultant CrO<sub>2</sub>/methyl methacrylate/methyl ethyl ketone mix along with an additional 83.4 parts of the original 5% by weight solution of polymethyl methacrylate in methyl ethyl ketone resulting in a formulation in which the final ratio of CrO<sub>2</sub> to polymethyl methacrylate was unity. This casting solution was laid down on 0.025 mm and 0.05 mm thick films of a commercially available polyethylene terephthalate at doctor knife settings at 0.1, 0.175 and 0.25 mm to give, after drying, final thicknesses of the CrO<sub>2</sub>-polymethyl methacrylate formulation of 0.006—0.0075; 0.01—0.013, and 0.015—0.017 mm, respectively.

##### Part C — Reflex Imaging with Visible Development.

A sample of one of the thinnest CrO<sub>2</sub>/

polymethyl methacrylate coatings, prepared as above, was observed optically and was found to consist of small, opaque regions of  $\text{CrO}_2$  particles about 0.5—5.0 microns in total agglomerate dimensions. The transmission optical density as measured using white light was 0.22.

The film was magnetized in a field of magnetic strength of 1000 gauss, and the magnetized film was placed (coating side down) in contact with a sheet of white paper containing a black printed image thereon. The reflectance optical density measured with white light was 0.06 for the background paper and 1.26 in the image, i.e., printed area of the original. A commercially available electronic photographic flash unit (an Ultrablitz (Registered Trade Mark) Cornet M flash unit, capacitance of 300 $\mu\text{f}$ ) was charged to 500 volts and discharged through the back of the topmost sheet of the assembly, i.e., the 0.05 mm transparent polyethylene terephthalate film base. The assembly was then separated.

The  $\text{CrO}_2$ -containing film was dipped in a powder suspension which consists of small particles of ferromagnetic material in a hydrocarbon solvent, removed, and then air-dried. The ferromagnetic particles of the suspension were found to adhere selectively to those regions of the  $\text{CrO}_2$ -containing film corresponding to the image areas of the original printed film. Thus, there was obtained a right-reading positive image of the original message as seen through the transparent polyester film. The  $\text{CrO}_2$ -containing film carrying the ferromagnetic image was then placed face down, i.e., with the image on the bottom, against a clear plastic sheet with a pressure-sensitive adhesive to transfer the ferromagnetic black particle image to the adhesive sheet. Simple pressure resulted, when the two films were separated manually, in the transfer of the ferromagnetic image from the  $\text{CrO}_2$  film to the plastic adhesive-coated film. The adhesive sheet with the thus transferred ferromagnetic image of the original message was then adhered to white paper to increase contrast. Resolution and fidelity were good. As long as the imaged  $\text{CrO}_2$  film is not remagnetized, it may be redeveloped by again dipping in the suspension of iron particles and transferring the iron particle image to the final copy paper. As many as 50 copies have been made with no loss in quality by this method. The  $\text{CrO}_2$  film may be completely erased for reuse by remagnetizing.

The formation of the right-reading positive image is especially surprising, in that the image is formed by light reflectance rather than as might be expected by planar heat contact. Thus, in the exposure step reading downwardly from the flash tube, there are in order the transparent polyethylene terephthalate film base, the  $\text{CrO}_2$ -containing poly-

methyl methacrylate layer, and the paper original containing thereon a printed black ink image.

When the flash tube is activated, the exposure necessarily goes first through the transparent film base and, in so doing, is substantially unaltered and substantially unabsorbed. In continuing its downward path, the flashed light next goes through the polymethyl methacrylate/ $\text{CrO}_2$  layer. The  $\text{CrO}_2$  being inherently of itself opaque absorbs some of the transmitted radiation and, in so absorbing, is heated to some degree. Thus, in its downward path, the flashed light transmitting the  $\text{CrO}_2$ -containing layer thermally biases the magnetized  $\text{CrO}_2$  towards demagnetization. In continuing its down path, the flashed light next hits the white background original containing the black printed message and the light is selectively absorbed in the black image areas and selectively reflected from the background or white areas of the original.

The intensity and exposure times of the flashed light are such that the heat buildup arising in the black image areas, by virtue of the absorption of the light therein, is not sufficient to effect enough heat buildup in said areas to transmit backwardly by thermal contact to the  $\text{CrO}_2$  layer and appreciably alter the magnetic properties of the  $\text{CrO}_2$  in those areas of that coating corresponding to the areas of the black original image.

On the other hand, the reflectance of the white background areas on the original is sufficiently high so that the transmitted light reaching these areas is reflected backward through the  $\text{CrO}_2$ -containing polymethyl methacrylate layer in sufficient intensity to result, after necessary absorption by the  $\text{CrO}_2$  particles, in a sufficient heat buildup in the  $\text{CrO}_2$  particles to raise the material above its relatively low Curie temperature and thereby demagnetize the  $\text{CrO}_2$  layer in those areas. Thus, surprisingly what is obtained is an image achieved by selective demagnetization by imagewise raising the temperature of the  $\text{CrO}_2$  layer above the Curie temperature of the premagnetized  $\text{CrO}_2$  particles, the imagewise demagnetization being achieved by a joint result of transmission thermal bias and imagewise reflectance absorption. Thus, the entire image-forming process, while admittedly involving light and operating through absorbed heat, does not depend on, and in fact preferably avoids, direct thermal transfer via contact.

#### EXAMPLE II.

A sample of  $\text{CrO}_2$ , prepared as described in general in Example I, Part A, with a saturation magnetization of 75 emu/g. measured at 4400 oersteds at 25° C. was ball-milled in water to break up aggregates, washed, and dried. A coating mixture was prepared by kneading in a polyethylene bag 10 parts of the just described, powdered  $\text{CrO}_2$ , 10 parts



of a high molecular weight polyvinyl chloride, 2 parts of a polymeric epoxy plasticizer/stabilizer, 5 cc. of cyclohexanone and 15 cc. of tetrahydrofuran. The resultant composition was then milled on a 15.2 cm rubber mill using additional tetrahydrofuran to maintain a desirable milling consistency until the  $\text{CrO}_2$  was completely incorporated into the solvent-plasticized polyvinyl chloride. There was thus obtained a plastic, flexible polymeric sheet.

This sheet was then dissolved in just over three times its weight of tetrahydrofuran and the resultant suspension cast on a 0.025 mm polyethylene terephthalate film base using a doctor knife setting of 0.025 mm. The cast film was then air-dried and resulted in a 0.0013 mm coating thickness of the dispersed  $\text{CrO}_2$  on the polyethylene terephthalate film base.

A sample of the just described flexible polyethylene terephthalate film carrying a dispersion of  $\text{CrO}_2$  in polyvinyl chloride was substantially uniformly magnetized with a 1000 cycle/second signal by passage through an Ampex (Registered Trade Mark) Model 600 magnetic tape recorder. The thus magnetized  $\text{CrO}_2$ -containing tape was placed (coating side down) in contact with a series of printed lines on white paper. The assembly was then exposed to the flash from an Ultrablitz Meteor SP electronic flash unit (capacitance, 600  $\mu\text{f}$ ) charged at 500 volts. After exposure and separation of the original and the  $\text{CrO}_2$ -containing film, it was found that the latter had been imagewise demagnetized by the exposure in the regions of the film corresponding to the white background areas of the original but remained substantially unchanged magnetically in the regions thereof corresponding to the image areas, i.e., the printed lines, in the original. As determined by suitable instrumentation, the amplitude of the signal obtained from the exposed  $\text{CrO}_2$  film member in the areas thereof corresponding to the background areas of the original was as low as 5 mv; whereas, the amplitude in the areas of the exposed film corresponding to the image areas of the original was approximately 40 mv.

#### EXAMPLE III.

A printing ink formulation was prepared from 35 parts of an alkyd for printing-ink use (Aroplaz 1271), 65 parts of  $\text{CrO}_2$  (magnetic properties: coercivity 415 oersteds, saturation magnetization 78.5 emu/g., measured at 4400 oersteds at 25° C., remanence 37.6 emu/g.), 5 parts of varnish (No. 00 transparent varnish) and 0.2 part of a lithographic ink drier (Maff paste).

The above was mixed on a three-roll mill operating with 22.68—45.36 kg. front-to-rear roll pressure for four passes over the rolls. The ink was then used on a letterpress to print from a 50% tint 118-line/cm plastic halftone printing plate onto a 0.13 mm thick

polyethylene terephthalate film. The ink film was then air-dried resulting in a coating thickness of .003 mm, exhibiting a transmission optical density to white light of 0.50.

The resultant printed film was magnetized in a 1500 gauss d.c. field and placed in direct contact on top of a printed resolution chart on paper containing 22 lines/cm as the maximum, with the  $\text{CrO}_2$  bearing surface of the printed film down in contact with the resolution chart. The reflectance optical density of the said resolution chart, again measured with white light, was 1.28 in the printed, line regions and 0.12 in the background regions. A 140 ufd capacitor bank was charged to 900 volts and discharged through a General Electric FT 91/L xenon flash lamp housed in a spherical reflector approximately 10.2 cm from the surface of the assembled sheets. The energy output of the lamp at this same distance was measured as 0.15 joule/cm<sup>2</sup> at the composite film surface.

The assembly was separated and the exposed  $\text{CrO}_2$ -containing film was dipped into a mixture of five parts of carbonyl iron in 200 cc. of fluorocarbon trichlorotrifluoroethane. The film was removed from the developing bath and air-dried. Carbonyl iron particles were found to adhere to the film in the regions thereof corresponding to the printed regions of the resolution chart. Thus, the developed iron image on the  $\text{CrO}_2$ -containing face was wrong-reading as viewed from said face but was right-reading as read through the transparent support. The 22-line/cm image of the original was clearly readable on the developed film. The  $\text{CrO}_2$ -containing developed film was then placed with the iron-developed image directly in contact with an adhesive-coated white paper with the adhesive coating in contact with the iron image. On mild pressure, the carbonyl iron image was transferred to the paper, thereby resulting in a right-reading image of the resolution chart with good fidelity and resolution. Multiple copies were made by repowdering the imagewise demagnetized film and transferring the resultant iron image.

#### EXAMPLE IV.

##### Effect of Thermal Biasing.

##### Part A — Preparation of $\text{CrO}_2$ film.

A 4.85% polymethyl methacrylate (PMMA) solution was prepared by dissolving 30 parts high molecular weight heat polymerized polymethyl methacrylate in 590 parts methyl ethyl ketone. The viscosity of the solution (Brookfield, No. 4 spindle, 50 rpm) was 680 centipoises. A dispersion was prepared by ball milling for 125 hours 10 parts of the  $\text{CrO}_2$  described in Example I, Part A and 103.3 parts of above PMMA solution. This 2/1  $\text{CrO}_2$ /PMMA dispersion was converted to a 1/5 dispersion by diluting 12.5 parts with 102 parts of the 4.85% PMMA solution. Viscosity of this dispersion (Brook-

field, No. 4 spindle, 50 rpm) was 620 centipoises.

5 A film was cast from the above 1/5 CrO<sub>2</sub>/PMMA dispersion onto a 0.05 mm polyethylene terephthalate film using a doctor knife setting of 0.08 mm. The resulting film, dried at room temperature, had a transmission optical density of 0.26 corresponding to a light transmission value of 55% (including 0.05 mm film substrate). The coating thickness was 0.005 mm.

#### Part B.

15 A capacitor was charged to voltages as indicated in Table I, following, and then triggered to discharge the capacitor through a General Electric FT-91/L flash lamp. This lamp was located horizontally 10.2 cm above a 7.6 cm diameter opening in a 17.8 cm

diameter spherical reflector. The energy stored in the capacitor is given by the formula 20

$$E = 1/2 CV^2,$$

where E is in joules, C is in farads, and V is in volts. The energy density arriving at the 7.6 cm diameter opening was measured by means of a Westinghouse laser radiometer, model RN-1. The housing of the radiometer was flush with the 7.6 cm diameter opening in the spherical reflector while the mica window of the radiometer was located 1.3 cm below the plane of this opening. The output of the laser radiometer was detected by means of a Keithly, model 149, milli-micro voltmeter. The resulting energy density in terms of millijoules/cm<sup>2</sup> is tabulated as a function of the capacitance and the voltage in Table I. 35

TABLE I

Energy Density from FT-91 with the 17.8 cm Spherical Reflector  
in Millijoules-Centimeter<sup>-2</sup>

Capacitance μf	Voltage					
	500	600	700	800	900	1000
5	0.56	0.86	1.25	1.76	2.39	3.14
10	1.45	2.23	3.15	4.30	5.69	7.28
20	4.43	6.5	9.2	12.8	17.2	23.0
40	8.5	14	20.8	29	38.3	50.6
60	13.5	21.7	31.5	44	60	82
80	22.0	33.3	47	62.8	82	104.5
100	28.5	43.3	61.0	81.8	106.0	134.7
120	38.8	55.0	75	100.0	129.5	164.0
140	45	65.5	89.8	118.0	151.2	189.2
160	54	77.4	105.0	138.0	176.8	221.0
180	—	86.0	118.5	155.5	196.4	239.4
190	—	89.0	126.0	167.0	211.0	256.5

40 A strip of the CrO<sub>2</sub>-coated film of Part A was cut into a 0.64 cm wide strip by 26.7 cm long and formed into a continuous loop 69.8 cm in circumference by splicing with leader tape. This loop was used with an Ampex F-44 tape recorder. A 700 cycles/second signal was recorded at 9.5 cm per second tape speed. The tape was removed and placed in contact with a piece of paper (white paper or black paper to

simulate white copy bearing black print images) with CrO<sub>2</sub> surface of the tape against the paper. The paper was directly in contact with an aluminum platen, heated electrically and controlled at the temperature indicated in Table II following, by a thermocouple embedded in the platen. A vacuum hold-down system was used to keep the paper and the tape in intimate contact with the platen. An opaque mask was used on top of the tape to 50  
55

limit the length along the tape of the area to be exposed. The 7.6 cm diameter opening in the spherical reflector containing the General Electric FT-91 flash tube was then brought into contact with the mask on the backside of the polyester supporting tape. The capacitor was then charged to the voltage indicated in Table II, and then discharged. The tape was next advanced and given a different exposure.

The exposed tape was then repositioned on the Ampex recorder. The signal was read out (played back) and displayed on a cathode ray tube. The percent reduction in amplitude of signal in the areas which had been exposed to the flash was used as a measure of the average percentage demagnetization that had taken place. This percentage demagnetization and the energy arriving at the surface of the  $\text{CrO}_2$  film are tabulated in Table II.

Data in Table II illustrate that the energy requirement imposed on the flash lamp may be reduced by approximately one-half the room temperature values at  $75^\circ\text{C}$ ., one-fifth the room temperature values at  $100^\circ\text{C}$ ., and one-twentieth the room temperature values at  $120^\circ\text{C}$ .

The controlling mensuration is the energy density at film (last column) since the necessary capacitance decreases with increasing temperature. Comparisons should be made between white-white and black-black copy papers. Also comparisons for equivalent ex-

posures should be made with respect to energy densities reported.

In addition to reducing the energy requirements as shown in Table II, thermal biasing gives a slight improvement in gray scale. The thermal biasing may be applied up to any temperature below the Curie temperature of the particular hard magnetic imaging particles used. Thus, for  $\text{CrO}_2$ , the Curie temperature is near  $119^\circ\text{C}$ . This varies somewhat depending on the modifiers used in the synthesis and the strength of the field used to magnetize, but Curie temperatures in the range of  $70^\circ\text{C}$ .— $170^\circ\text{C}$ . are attainable with modified  $\text{CrO}_2$ . It will be appreciated that the use without thermal biasing of a modified chromium dioxide with a Curie temperature near  $70^\circ\text{C}$ . would be approximately equivalent to thermally biasing at about  $75^\circ\text{C}$ . the usual chromium dioxide with Curie temperature of  $119^\circ\text{C}$ . The particular choice of thermal biasing conditions, of course, will depend on the rate of decay of magnetic properties with increasing temperature for the hard magnetic particles involved, and the temperature limitations imposed by stability of the nonmagnetic binder, if used, for the magnetic particles and of the transparent supporting member upon which the particles are coated or printed. Thermal biasing may be established by direct contact with a heated platen as in the examples above or by other obvious means.

TABLE II

Temperature	Color of Copy Paper	Capacitance	Voltage	% Demag.	Energy Density at Film millijoules/cm <sup>2</sup>
Room	White	140 $\mu\text{f}$	950	96	170
			900	76	151
			850	41	134
	"	160 $\mu\text{f}$	1000	100	221
			900	96	177
			800	26	138
	"	140 $\mu\text{f}$	1000	100	189
			900	65	151
			800	0	118
	"	120 $\mu\text{f}$	1000	88	164
			900	28	130
			800	0	100
	"	100 $\mu\text{f}$	1000	51	135
			900	7	106
			800	0	82

TABLE II (cont.)

Temperature	Color of Copy Paper	Capacitance	Voltage	% Demag.	Energy Density at Film millijoules/cm <sup>2</sup>
Room	Black	190 $\mu$ f	1000	86	257
			950	43	229
			900	20	202
	„	180 $\mu$ f	1000	78	239
			900	14	196
	„	160 $\mu$ f	1000	50	221
			900	9	177
			800	0	138
	„	160 $\mu$ f	1000	59	221
			950	18	198
			900	7	177
75° C.	White	40	1000	29	51
			700	0	47
		120	600	0	55
			600	16	66
		120	700	63	75
			750	51	71
	„	80	1000	100	104
			900	93	82
			800	50	63
		60	1000	87	82
			900	58	60
			800	9	44
	Black	60	1000	16	82
			900	0	60
			800	0	44
		80	1000	68	104
			900	24	82
			800	4	63
	„	100	1000	94	135
			900	59	106
			800	13	83
		100	1000	100	164
			900	92	129
			800	41	100

TABLE II (cont.)

Temperature	Color of Copy Paper	Capacitance	Voltage	% Demag.	Energy Density at Film millijoules/cm <sup>2</sup>
100° C.	White	80	600	55	33
	"	40	850	60	33
	"	40	800	48	29
	"	40	750	23	25
			700	14	26
	"	40	1000	100	51
	"	60	800	91	44
	"	80	700	88	47
	"	40	1000	95	51
			900	81	38
			800	41	29
	"	20	1000	5	22
			900	0	18
			800	0	13
	Black	40	1000	64	51
			900	35	38
			800	0	29
	"	60	1000	95	82
			900	82	60
			800	55	44
	"	60	800	39	44
			700	13	35
110° C.	White	20	1000	70	22
	"	20	900	53	18
			800	19	13
		20	800	21	13
			700	10	9
			600	6	6
	"	40	1000	100	51
			900	100	38
			800	94	29
	Black	40	1000	96	51
			900	84	38
			800	46	29
	Black	20	1000	44	22
			900	13	18
			800	6	13

TABLE II (cont.)

Temperature	Color of Copy Paper	Capacitance	Voltage	% Demag.	Energy Density at Film millijoules/cm <sup>2</sup>
120° C.	White	10	1000	80	7.3
	"	10	1000	57	7.3
			900	45	5.7
	"	10	800	29	4.4
			700	7	3.2
			600	0	2.2
	"	20	1000	100	22
			900	95	18
			800	75	13
	"	20	700	62	9.2
			600	30	6.3
	Black	20	1000	91	22
			900	80	18
			800	69	13
	"	20	700	19	9.2
			600	0	6.3

## WHAT WE CLAIM IS:—

1. A thermomagnetic copying process which comprises exposing to actinic radiation by reflex exposure as hereinbefore defined from a document, a magnetic recording member comprising fine discrete particles of a size of 0.01 to 5.0 microns of a material capable of magnetisation to a hard magnetic state, having an energy product  $(BH)_{max}$  of 0.08—8.0 gauss oersteds  $\times 10^6$ , a remanence  $B_r$  of 500—21,500 gauss, a coercivity  $H_c$  of 40—6,000 oersteds and a Curie temperature not exceeding 1,200° C., contained in a stratum carried by a support, the whole being transparent to a degree sufficient to transmit at least 2% of actinic radiation, the intensity of the exposure being such that in the areas corresponding to the more reflective areas in the document the temperature of the magnetic material is raised above its Curie temperature, while in the areas corresponding to the less reflective areas it remains below the Curie temperature, while maintaining the recording member in a state such that its magnetic state will change above, but not below, the Curie temperature, and reading out the resulting magnetic image.
2. A thermomagnetic copying process which comprises
  - (1) placing over a document to be copied a magnetised recording member which has a degree of transparency sufficient to transmit at least 2% of actinic radiation and which comprises discrete particles of a size of 0.01 to 5.0 microns of a material capable of magnetisation to a hard magnetic state having an energy product  $(BH)_{max}$  of 0.08—8.0 gauss oersteds  $\times 10^6$ , a remanence  $B_r$  of 500—21,500 gauss, a coercivity  $H_c$  of 40—6,000 oersteds and a Curie temperature not exceeding 1,200° C., contained in a stratum carried by a support,
  - (2) selectively demagnetising the magnetised stratum by exposing it to actinic radiation by reflex exposure, as hereinbefore defined, of intensity such that its temperature in the areas corresponding to the more reflective areas of the document is raised above its Curie temperature, causing such areas to be demagnetised to a degree proportional to the reflectivity of the reflective areas of the document, while the areas corresponding to the less reflective areas of the document retain their magnetisation substantially unchanged, and
  - (3) reading out the resulting magnetic image.
3. A process according to claim 1 or 2, wherein the recording member is flexible.
4. A process according to any one of the preceding claims, wherein the particles are dispersed in a polymeric binder in the form



of a stratum 0.003 to 0.13 mm thick, carried on a support.

5 5. A process according to any one of the preceding claims, wherein the magnetic material has a Curie temperature of 25°—500° C.

6. A process according to any one of the preceding claims, wherein the magnetisable material is chromium dioxide.

10 7. A process according to any one of the preceding claims, wherein the recording member transmits from 50 to 90% of the exposing actinic radiation.

15 8. A process according to any one of the preceding claims, wherein a copying member comprising a transparent polymeric film carrying a layer of premagnetised fine discrete particles of a material capable of magnetisation to a hard magnetic state in a polymeric binder is placed in contact with a sheet of white paper carrying a black or coloured printed image, and a photographic flash tube is discharged through the assembly.

25 9. A process according to any one of the preceding claims, wherein the resulting magnetic image is rendered visible by applying to it a ferromagnetic powder and removing the powder from the unmagnetised areas.

30 10. A process according to claim 9, wherein the resulting visible image is transferred to a receptor surface.

35 11. A process according to claim 10, wherein the ferromagnetic grains have a thermoplastic coating and the image is transferred to a paper receptor by heating.

12. A process according to any one of the preceding claims, wherein the support is a polyethylene terephthalate film.

13. A thermomagnetic copying process

according to claim 1 or 2 substantially as hereinbefore described.

14. A copying member suitable for use in the process of any one of the preceding claims, comprising a magnetic stratum which contains a hard magnetic material of particle size 0.01 to 5.0 microns and which can transmit at least 2% of actinic radiation falling on it and having an energy product (BH) max of 0.08—8.0 gauss oersteds  $\times 10^6$ , a remanence of B

of 500—21,500 gauss, a coercivity  $H_c$  of 40—6,000 oersteds and a Curie temperature not exceeding 1,200° C.

15. A copying member according to claim 14, wherein the magnetic material is non-uniformly dispersed in the stratum and is non-uniformly agglomerated, with agglomerates ranging up to 0.25 mm. in maximum dimension.

16. A copying member according to claim 14 or 15, wherein the magnetic material is chromium dioxide.

17. A copying member according to any one of claims 14—16, wherein the magnetic material is premagnetised.

18. A copying member according to any one of claims 14—17, wherein the magnetic stratum is in the form of a dot/screen pattern.

19. A copying member according to any one of claims 14—18, wherein the magnetic stratum is carried on a flexible support.

20. A copying member according to claim 14 substantially as hereinbefore described.

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